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UNITED STATES PATENT APPLICATION

of

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for

<u>EXTENDED TEMPERATURE RANGE EMF DEVICE</u>

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Field Of The Invention

[0001] The present invention relates to sensors which generate an EMF in the presence of a temperature gradient between the terminal ends of the sensor.

Background Of The Invention

[0002] Thermocouples are temperature measuring devices which measure temperature by employing dissimilar metal conductors joined at a point or junction where the temperature is to be measured with free ends connected to an instrument to measure a voltage generated across the junction of the dissimilar metals. The bimetallic junction of dissimilar metals has been formed of various metals which provide a thermoelectric differential between the two metals upon exposure to heat.

[0003] Conventional devices use a variety of materials to produce thermocouple sensors with high operating temperatures. The various metals used to form thermocouple sensors suffer from the detrimental effects of contamination, ionic migration, sublimation, oxidation and substantial decrease in mechanical strength with increasing operating temperatures. Current sensors are thus limited to an operating envelope of less than 1090 °C (1994 °F) to ensure long term, stable output with minimum drift in resistance. Higher temperature sensors can operate to temperatures up to 2370 °C (4298 °F) but are either limited to specific environmental conditions (such as for instance: a vacuum environment, an inert gas environment, or a hydrogen atmosphere) and/or must be limited to short term operation to prevent premature failure. This temperature operating range has limited the application of these sensors in hostile, high temperature systems such as

those commonly encountered in the aerospace, petroleum and glass industries.

[0004] Prior art thermocouple sensors have had the disadvantage of melting at fairly low temperature and have required insulation and various sheathing systems to protect the thermocouple during operation at prolonged elevated temperatures. However, this sometimes results in undesirable reactions between the metals in the thermocouple sensor and the materials used in the insulation and sheathing systems.

[0005] The problems of undesirable reactions in thermocouple sensors have been aggravated by the temperatures encountered in nuclear reactor systems, rocketry heat sensors, high-temperature and vacuum processing and other applications where temperature measurements at or above 1500 °C (2730 °F) are involved. Thermocouples have utilized sheathing and insulation in an effort to prevent the disintegration of the thermocouple in such systems. The insulation and sheathing systems have the further disadvantage of resulting in time delays in obtaining temperature readings due to the insulation and mechanical packaging designed implemented to prevent failure resulting from such problems as gas leakage at the thermocouple sheath seals, cracked sheaths and other mechanical limitations imposed by ceramic insulated metal sheathed thermocouple sensors.

[0006] Prior art bimetallic bare sensor combinations, such as those formed from tungsten and rhenium have generally not proven to be uniformly reliable or to have a useful operational life at extended temperatures due to breakage of the thermocouple hot junction upon initial heating and drifts in EMF temperature relationships. These problems are believed to be the result of thermal and chemical phase transitions and of preferential evaporation of one of the metals in the bimetallic sensor. These sensors are thus limited to vacuum, inert, or hydrogen atmospheres.

[0007] High melting, noble metal thermocouples made of e.g., platinum (Pt), rhodium (Rh), palladium (Pd), iridium (Ir) and alloys thereof are known in the art. For example, some widely used thermocouples for measurement of temperatures above 1000 °C (1830 °F) are: (Pt / Pt - 13% Rh); (Pt / Pt - 10% Rh); and (Pt - 6% Rh / Pt - 30% Rh). Each leg of the thermocouple is made of a wire or thin film of Pt and/or Pt – Rh. The EMF-temperature responses for these devices, the basis of temperature measurement via thermocouples, are moderate and oxidation resistance is good. These thermocouples can be used with moderate to severe drift (i.e., a change in EMF with time due to any cause such as composition change, oxidation or chemical attack) up to 1500 °C (2730 °F). Other noble metal elements, e.g., palladium and iridium, and precious metal elements, e.g. gold and silver or alloys thereof with platinum are also useful to form thermocouples. Such thermocouples, however, are not widely used because they are more susceptible to oxidation than platinum, and degrade by drift caused by selective oxidation.

[0008] Some of the characteristics of platinum can be improved by the usual alloy hardening method of adding a metal to the platinum base, followed by heat treatment. However, problems can occur after alloying. For example, when a high concentration of any alloying element is added to the platinum base, the electrical properties of the resulting platinum limb become inferior; at the same time the hardening phase will partially or totally dissolve into the base at high temperatures, thus the effects of the hardening action will be reduced.

[0009] The prior art attempts to extend the operation range of thermocouples have been limited to extending the range of known thermocouple material through the use of insulation and sheathing techniques or increasing the high temperature properties of known materials through alloying processes or coatings. The disadvantages of these techniques,

including not reaching a high enough operating temperature, are discussed above. A significant benefit, however, is that the conversion of the output signal generated by the known thermocouple materials is readily available through National Institute of Standards and Technology (N.I.S.T.) or International Electrotechnical Commission (I.E.C.) standard tables.

[0010] Conversely, if a thermocouple material was chosen based on its desired high temperature operating properties, and not based on providing a known EMF output, then higher operating range thermocouples could be made, provided that the output signal of the thermocouple material is repeatable and convertible.

[0011] Dispersing oxides of transition metals or rare earth metals within noble or precious metals is an example of a method of creating thermocouple materials with the desired extended temperature properties. For instance, dispersion hardened platinum materials (Pt DPH, Pt-10%Rh DPH, Pt-5%Au DPH) are useful materials because they achieve very high stress rupture strengths and thus permit greatly increased application temperatures than the comparable conventional alloys.

[0012] Dispersion hardening (DPH) creates a new class of metal materials having resistance to thermal stress and corrosion resistance that is even greater than that of pure platinum and the solid solution hardened platinum alloys. When operational life, high temperature resistance, corrosion resistance and form stability are important, a sensor can be manufactured of DPH platinum and can be used at temperatures close to the melting point of platinum.

[0013] Dispersion hardened materials contain finely distributed transition element oxide particles which suppress grain growth and recrystallization even at the highest temperatures and also hinder both the

movement of dislocations and sliding at the grain boundaries. The improved high temperature strength and the associated fine grain stability offer considerable advantages.

[0014] DPH of platinum has been developed and applied to for instance, the glass industry. For instance, zirconia grain stabilized platinum has been used in the glass industry for the construction of a sheet of material. This approach however, has not previously been used in the measurement field. For instance, the glass industry is focused on stability of the material at high temperature, whereas in the measurement field not only is material stability at high temperature a concern but signal repeatability and quality are critical. In addition, the various DPH of platinum approaches taken have utilized a powder material that cannot be utilized and manufactured into a wire for use in a measurement device. Therefore, these techniques are not usable for the measurement field.

[0015] Platinum: Platinum-Rhodium Thermocouple Wire: Improved Thermal Stability on Yttrium Addition Platinum, By Baoyuan Wu and Ge Liu, Platinum Metals Rev., 1997, 41, (2), 81-85 is incorporated by reference. The Wu article discloses a process of dispersion hardening platinum for a platinum / platinum-rhodium thermocouple wire which incorporates traces of yttrium in the platinum limb.

[0016] As described in the Wu article, the addition of traces of yttrium to platinum as a dispersion phase markedly increases the tensile strength of the platinum at high temperature, prolongs the services life and improves the thermal stability. Yttrium addition prevents the growth in the grain size and helps retain the stable fine grain structure, as the dispersed particles of high melting point resist movements of dislocations and make the materials harder. The strength of a material is related to the movement and number of the dislocations.

[0017] In order to harden metals, the movement of the dislocations needs to be restricted either by the production of internal stress or by putting particles in the path of the dislocation. After the melting and annealing process, the majority of the trace yttrium (in the dispersion phase of the platinum) becomes yttrium oxide, which has a much higher melting point than platinum. When the temperature is near the melting point, dispersion hardened particles fix the dislocation, thus hardening the platinum and increasing its strength.

[0018] At the same time the grain structure becomes stable after dispersion hardening and there is also microstructural hardening. The dispersed particles affect the recrystallization dynamics, inhibit rearrangement of the dislocations on the grain boundaries and prevent the movement of the grain boundaries. Therefore, this dispersion hardened platinum possesses a stable fine grain structure at high temperature.

[0019] The Wu thermocouple meets the output requirements of the Type S standard for thermocouples – those made of Pt: Pt-10% Rh – whose manufacturing tolerances are prescribed by the International Electrotechnical Commission (I.E.C.). Because the platinum-rhodium leg of a conventional thermocouple has much higher tensile strength than a pure platinum leg, the Wu thermocouple dispersion hardened only the platinum leg in order to increase the tensile strength of the platinum leg to balance the strength of the two legs. The Wu thermocouple did not use dispersion hardening in both legs and did not face the challenge of obtaining a repeatable output signal from the thermocouple at an extended range.

[0020] This patent outlines a thermocouple sensor capable of extending the operating range of this class of sensor up to 1700 °C (3092 °F).

Summary Of The Invention

[0021] Accordingly, it is an object of the present invention to provide an extended temperature range EMF device with enhanced high temperature operating characteristics and long term, stable output and minimum drift in EMF.

[0022] Another object of the present invention is to provide an extended temperature range EMF device that can be configured as a thermocouple for the purpose of measuring localized temperature. Still another object of the present invention is to provide a device which in inverse mode operation can be used as a voltage generator in the presence of a temperature gradient.

[0023] Yet still another object of the present invention is to provide an extended temperature range EMF device which in dual mode operation can be implemented as a heat flux sensor. A further object of the invention is to provide a device which can be a part of a parallel array of devices to create a thermopile of increased sensitivity or voltage output.

[0024] And still yet another object of the present invention is to provide an EMF device implementing electronics to condition the output and convert it to specified calibrated reference data, or to an industry standard such as a National Institute of Standards and Technology reference or an International Electrotechnical Commission reference.

[0025] And yet another object of the present invention is to provide a method for the production of a cost effective, high reliability, stable EMF devices with an operating range of up to 1700 ˚C (3092 ˚F) in hostile environments.

[0026] These and other objects of the present invention are achieved by providing a sensor which is resistant to degradation at high temperature having two components in contact with each other, with two conductive leads for transmitting an electric signal. The first component is formed of at least one first noble metal and an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these, while the second component is formed of at least one second noble metal, different than the first noble metal, and an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these.

[0027] The objects of the present invention are further achieved in another embodiment by providing a sensor which is resistant to degradation at high temperature having two components in contact with each other, each component capable of transmitting an electric signal. The first component is formed of an oxide selected from the group consisting of transition element oxides and rare earth metal oxides, and combinations of these, where the oxide is dispersion hardened within the grain boundary and within the main body of a first base metal selected from the group consisting of the noble metals and the precious metals, and combination of these. The second component is formed of an oxide selected from the group consisting of the transitional metal oxides and the rare earth metal oxides, and combinations of these, where the oxide is dispersion hardened within the grain boundary and within the main body of a second base metal, that is different from the first base metal, selected from the group consisting of the noble metals and the precious metals, and combination of these.

[0028] The objects of the present invention are achieved in yet another embodiment by a method of manufacturing a high temperature resistant sensor by forming a first component from at least one first noble metal and an oxide selected from the group consisting of yttrium oxide, cerium

oxide, zirconium oxide, and combinations of these and a second component from at least at least one second noble metal, different than the first noble metal, and an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these. Next, joining said first and second components and attaching a pair of leads connected one each to the first and second component for transmitting electrical signals.

[0029] The objects of the present invention are further achieved in another embodiment by providing a sensor which is resistant to degradation at high temperature having a first and second component, each adapted to transmitting an electrical signal. The first component is formed of an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these, where the oxide is dispersion hardened within the grain boundary and within the main body of platinum. The second component formed of an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these, where the oxide is dispersion hardened within the grain boundary and within the main body of a platinum rhodium alloy. This sensor also has a transducer to receive an electrical signal.

[0030] The objects of the present invention, in each of the above described embodiments, could be further achieved where an electrical signal comprises a varying voltage and is applied to a transducer. The transducer may be a temperature measuring device. The output of the transducer may correlate to a temperature or a logic function applied to specific calibration data to determine the temperature. The transducer output could correlate to a standard reference output, or could correlate specifically to a National Institute of Standards and Technology or to an International Electrotechnical Commission reference.

[0031] The objects of the present invention, in each of the above described embodiments could be additionally achieved where an electrical signal comprises a varying voltage and is applied to a transducer. The transducer may be a conditioner. The output of the conditioner may be a conditioned varying voltage which is adapted to power electronics.

[0032] In still another advantageous embodiment a modular sensor system for generating and sending a signal from a sensor to a transducer is provided comprising, a sensor for generating a signal, the sensor having, a first component comprising at least one first noble metal and an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations thereof, said first component further having a first conductor electrically connected thereto. The sensor also has a second component in contact with said first component, said second component comprising at least one second noble metal, different than the first noble metal, and an oxide selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations thereof, said second component further having a second conductor electrically connected thereto. The system further comprises a transmit lead module for transmitting the signal to the transducer, the transmit lead module having, a first transmit lead electrically connected to the first conductor, and a second transmit lead electrically connected to the second conductor, the second transmit lead comprising a different material than the first transmit lead. The transmit lead module also has an insulating layer within which the first transmit lead and the second transmit lead are located, and an outer layer within which the insulating layer is located.

[0033] In yet another advantageous embodiment a modular sensor system for generation of a signal by a sensor and for sending of the signal via first and second electrical conductors to a transducer is provided comprising, a transmit lead module for transmitting the signal to the transducer. The

transmit lead module has a first transmit lead electrically connected to the first conductor, a second transmit lead electrically connected to the second conductor, the second transmit lead comprising a different material than the first transmit lead. The transmit lead module also has an insulating layer within which the first transmit lead and the second transmit lead are located, and an outer layer within which the insulating layer is located, the outer layer comprising the same material as the first transmit lead.

[0034] The invention and its particular features and advantages will become more apparent from the following detailed description considered with reference to the accompanying drawings.

Brief Description Of The Drawings

[0035] FIG. 1 is an illustration of the system according to one advantageous embodiment of the present invention.

[0036] FIG. 1A is an illustration of a transmit lead module according to FIG. 1.

[0037] FIG. 2 is a view of the component set up for another embodiment of the present invention illustrated in Figure 1.

[0038] FIG. 3 is a view of the component set up for yet another embodiment of the present invention illustrated in Figure 1.

[0039] FIG. 4 is a view of the component set up for yet another embodiment of the present invention illustrated in Figure 1.

Detailed Description Of The Drawings

[0040] Referring to Figures 1 – 4, a sensor 10, is made of components of a class of materials chosen to be resistant to degradation in high temperature operation up to 1700 °C (3092 °F). The first component 11 and the second component 12 are dissimilar materials within a class. The class of materials is made up of one or more base metals, usually a noble metal, with metal oxides selected from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these. Through an annealing process not described herein, the metal oxides may be deposited within the grain boundaries and main body of the base metal. The process is called dispersion hardening. This has the effect of stabilizing the grain structure of the material at extended temperatures and provides an increased resistance path for impurities. The net effect is a highly stable material capable of withstanding mechanical loads and chemical attacks at elevated temperatures while maintaining its internal chemical integrity. This provides the foundation for an extended temperature range EMF device with long term, stable output and minimum drift in EMF.

[0041] The base metal may be chosen from the noble metals such as for instance, from the platinum group metals. In one preferred embodiment the first component 11 comprises platinum, having yttrium oxide or yttrium and zirconium oxide dispersed within its grain boundary and within the main body. In another preferred embodiment the second component 12 comprises a platinum rhodium alloy (10% rhodium) having yttrium oxide or yttrium and zirconium oxide dispersed within its grain boundary and within the main body.

[0042] The basic shape of components 11, 12 is not limited. The components can have a variety of cross sectional geometries as desired for the particular application. Furthermore, the components may be manufactured by depositing the material onto a substrate. The substrate may

comprise the same class of material as the components, having at least one noble metal with a metal oxide from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these, dispersed within its grain boundary and within the main body. Refractory materials of varying compositions such Al_2O_3 or MgO may also be used as the substrate.

[0043] Many varying structures may be utilized to for components 11, 12. All that is necessary is that the components contact each other such that they share a joined hot section 19. In addition each component must also have a cold junction end. In one advantageous embodiment, electrical leads 23, 24 for transmitting electrical energy, may be electrically connected between each cold junction end and a transducer/conditioner 15. In addition, transmit leads 13, 14 may comprise different material compositions than the electrical leads 23, 24 creating a junction at 17, 18. Another possible junction point 25, 26 may comprise still another differing material composition than the transmit leads 13, 14. However, the sensor could be formed such that one or both of the wire components may transmit electrical energy to the transducer/conditioner 15. It should also be noted that the electrical energy may be electrically compensated for these junction points of differing compositions.

[0044] The components of the sensor may also be housed in a sheath 20 to protect the device from the hostile environments in which the sensor operates. The sheath 20 may be formed of a high temperature alloy or made from the same class of material as the components, having at least one noble metal with a metal oxide from the group consisting of yttrium oxide, cerium oxide, zirconium oxide, and combinations of these, dispersed within its grain boundary and within the main body.

[0045] As depicted in Figure 1, the sensor may be insulated between the components 11, 12 and the sheath 20. The insulation 21 may be a refractory ceramic material such as Al_2O_3 or MgO.

[0046] In operation, the components of the sensor are exposed to a temperature gradient ΔT. The first component 11 interacts with the second component 12 at the joined hot section 19 such that electrical energy/signal or EMF is generated based upon the temperature gradient ΔT. The electrical signal may comprise, for instance, a varying voltage (Δv). The electrical signal may then be transmitted to the transducer/conditioner 15.

[0047] In one advantageous embodiment illustrated in Figure 1, electrical leads 23, 24 terminate at junctions 17, 18 respectively. From junctions 17, 18 transmit leads 13, 14 extend to junction point 25, 26 to terminate at transducer/conditioner 15. In Figure 1, transmit leads 13, 14 are illustrated located inside transmit lead module 30.

[0048] The structure and method for manufacturing transmit lead module 30 in one advantageous embodiment as illustrated in Figure 1A, will now be described. Transmit lead module 30 generally comprises: transmit leads 13, 14; insulating layer 32; and outer layer 34. Transmit leads 13, 14 may comprise any suitable materials as previously described herein in connection with Figure 1. Insulating layer 32 may comprise, for instance, a refractory ceramic material such as Al_2O_3 or MgO generally formed into an elongated member such as a cylinder. Also illustrated in Figure 1A are two through holes 36, 38 extending axially through the length of insulating layer 32 through which transmit leads 13, 14 are respectively inserted. Surrounding and encasing insulating layer 32 is outer layer 34. Outer layer 34 may comprise in one advantageous embodiment, the same material as one of transmit leads 13, 14. One advantage realized from this particular

configuration is that one of the electrical lead/transmit lead cold junctions may be eliminated.

[0049] Once the insulating layer 32 containing transmit leads 13, 14 is inserted into outer layer 34, the entire transmit lead module 30 may be swaged or drawn. The compression of transmit lead module 30 causes insulating layer 32 to be compressed and tightly crushed such that air is evacuated and any air pockets within transmit lead module 30 may be effectively eliminated.

[0050] Any number of transmit lead modules 30 may then be tied together depending upon the distance between the sensor and the transducer/conditioner 15. This provides versatility and modularity to the system as the installer may utilize any number of transmit lead modules 30 in an installation. Transmit lead modules 30 may further be bent and manipulated as desired to custom fit a particular installation. The outer layer 34 being rigid further provides protection for transmit leads 13, 14 from wear, abrasion and repeated bending and/or flexing. This will increase the effective lifespan of the system. In addition, as previously discussed, transmit lead modules 30 may be joined together with each other in an end-to-end fashion with transmit leads 13, 14 in the first transmit lead module 30 forming a junction with transmit leads 13, 14 in the second transmit lead module 30. However, when the exterior layer 34 for both the first and second transmit lead modules 30 comprises the same material as one of the transmit leads 13, 14, then the corresponding transmit lead junction may be eliminated further simplifying the system.

[0051] Whenever transmit leads are joined of differing composition this creates a potential for a secondary, tertiary, etc. EMF voltage which reacts with the primary EMF resulting in a shift in output. To maintain the maximum accuracy the cold junction temperature must be measured with an

external EMF device whose output is used to correct for the error either by an external user device or implemented in the logic function.

[0052] If the sensor is arranged as a thermocouple for the purpose of measuring localized temperature, the varying voltage will correlate to a temperature. The output from the transducer would then be a temperature reading from a temperature measuring device 16. (Figure 2). Certain reference conversions exist to determine temperature from a varying voltage output from a thermocouple. These standards are determined by such agencies as the National Institute of Standards and Technology and the International Electrotechnical Commission. The standards are based upon the properties of the material of the thermocouple components and the temperature ranges to which the thermocouple is subjected.

[0053] No standard reference to correlate the varying voltage to a temperature reading is available for the class of materials used in the present invention. Accordingly, a logic function 40 (Figure 3) can be applied to the varying voltage to convert it to one of the known industry standards and corrects for cold junction potential generated or created at junction 17, 18 and/or the transition at junction point 25, 26. This would make the thermocouple an off the shelf component.

[0054] The output of the sensors need not be converted to an NIST standard to make it usable. In some applications, calibration data can be supplied along with a basic algorithm which would be implemented in a control system developed by an outside source. In this case the algorithms would be customized to the user's particular application.

[0055] In inverse mode operation, the sensor can be used as a voltage generator in the presence of a temperature gradient. The varying

voltage output could be conditioned as a power source 41 to power electronics negating the need for an internal power supply. (Figure 4).

[0056] In dual mode operation, the sensor could be implemented as a heat flux sensor. Under either application, measuring temperature or as a voltage generator, the sensor could be configured as a part of a parallel array of sensors to create a thermopile of increased sensitivity or voltage output.

[0057] Those skilled in the art may tailor the present invention to suit a particular requirement. It will be understood that these or other types of changes and substitutions may be made within the spirit and scope of the invention as defined in this claim.